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VARIATION IN SHELL 405 CATALYST PHYSICAL
CHARACTERISTICS, TEST CATALYST
PREPARATION

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Shell Development Company

Prepared for:

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This report describes the continuation of a study for the Air Force Rocket Propulsion Laboratory to develop a catalyst of the Shell 405 type with improved durability to repeated cold starts using monopropellant hydrazine. Besides furnishing some standard grades of Shell 405 Catalyst, three experimental catalysts containing 36%, 44%, and 55% iridium were prepared for evaluation by the AFRPL.

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VARIATION IN SHELL[®] 405 CATALYST PHYSICAL CHARACTERISTICS

Test Catalyst Preparation

Sponsoring Agency:

Air Force Rocket Propulsion Laboratory
Air Force Systems Command

Contract No. F04611-72-C-0077

Final Report

Reported by: W. L. Petty
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A Division of Shell Oil Company
Houston, Texas

FOREWORD

This work was done by Shell Development Company for the Air Force Rocket Propulsion Laboratory under Contract F04611-72-C-0077. It was initiated 15 May 1972 and completed 31 May 1973. The effort was started at the Shell Laboratories in Emeryville, California, and was continued at the Shell Laboratories in Houston, Texas.

The work under the contract was supervised by Dr. W. L. Petty. The experimental studies and catalyst preparations were carried out by Mr. Yosh Sakauye.

The work was conducted under the technical management of Capt. Ronald J. Meetin of the AFRPL/LKDP.

This technical report has been reviewed and is approved.

Ronald J. Meetin, Capt., USAF
Project Engineer

ABSTRACT

This report describes the continuation of a study for the Air Force Rocket Propulsion Laboratory to develop a catalyst of the Shell 405 type with improved durability to repeated cold starts using monopropellant hydrazine. Besides furnishing some standard grades of Shell 405 Catalyst, three experimental catalysts containing 36%, 44%, and 55% iridium were prepared for evaluation by the AFRPL.

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VARIATION IN SHELL 405 CATALYST PHYSICAL CHARACTERISTICS

Introduction

The development of Shell 405 Catalyst made practical the use of hydrazine as a high energy monopropellant in trusters for space vehicles, and in gas generators for a variety of auxiliary and emergency functions. Over the years the inherent simplicity and other advantages of the hydrazine-catalyst system has led to growing use of Shell 405 Catalyst, notably in space applications. The present study was prompted in part by the possibilities of extending the uses of Shell 405 Catalyst and hydrazine into applications in which the requirements would surpass the limits of reliable performance of the current catalyst, but that might be met by a longer-life or otherwise more durable modification.

The NASA-sponsored study¹⁾ that led to Shell 405 Catalyst was directed toward finding a catalytic agent which would initiate hydrazine decomposition, have short ignition delay and multiple restart capability at low temperatures, and have good thermal and mechanical stability. Catalyst performance was measured by a liquid hydrazine activity test and by short-duration test firings in a small reactor.

The present study, sponsored by the AFRPL, was directed toward improving the operating life of the catalyst, measured by its maximum repetitive cold start capability. Most of the catalysts prepared for this study with different supports or under different than standard process conditions were prepared under AFRPL contract F04611-70-C-0020 (see Reference 2). Some additional samples with adjusted iridium metal loadings or processing techniques (reduction and decomposition) were to be made on the present contract. However, only five samples, three with different metal loadings and one standard laboratory and one plant production catalyst were requested. These were prepared by Shell Development Company and were evaluated through engine firings and laboratory activity tests at AFRPL.

Catalyst Preparations

All of the test catalysts (except the standard plant product) were prepared in the laboratory in accordance with established Shell 405 Catalyst manufacturing procedures and quality control, except for modifications in apparatus and conditions that were necessary for small-scale preparations. Besides the standard laboratory preparation (11724-114) containing 31.6% iridium, three other experimental catalysts were prepared containing 35.5%, 44.2% and 55.1% iridium, respectively (11724-110 to 112). Early results of performance tests on catalysts with high levels of metal indicated improved life; it appeared that these three additional samples would help in optimizing the iridium content.

Catalyst Analyses and Properties

The composition and physical data for these catalysts are summarized in Table 1 along with similar data for one standard plant product, another standard laboratory product made in the earlier work²⁾, and the Reynolds RA-1 alumina support used to prepare these catalysts. A summary of test methods is given in Appendix II. In addition, the plots of Adsorptomat measurements for the three experimental catalysts 11724-110 to 112 appear in Appendix III.

Based on the data shown in Table 1 of this report and in Table 2 of the earlier report²⁾, it appears that hydrogen chemisorption reaches a maximum at an iridium level of about 33%.

Recommendations

Performance loss in a monopropellant hydrazine/catalyst engine occurs by catalyst break-up and loss out the nozzle and/or by catalyst deactivation. Shell 405 Catalyst was developed primarily to give multiple cold starts, and the best support for this catalyst necessarily had high surface area. A catalyst which would be more resistant to attrition can presumably be made from a harder support than Reynolds RA-1 alumina, but high surface area (and activity) probably must be sacrificed to achieve this. Some engine firing results suggest that a major cause of catalyst break-up results from internal pressures which develop inside the catalyst pores during cold starts or periods of heavy bed-loading. Experiments can be designed and should be performed to demonstrate whether this is so. Positive results would clearly indicate a need for a trade-off between cold starts and high bed loading on the one hand and long life on the other.

Table 1. Composition and Physical Data of Support and Catalysts

Number	Material	Iridium %w	Adsorption Data						Hydrogen Chemisorption, μ Moles/g	Bulk Dens., g/cc
			Sur- face area, m^2/g	Pore Vol. cc/g	Vol. Avg. Diam., Angs.	Area Avg. Diam., Angs.	Vol. Median Diam., Angs.	Area Median Diam., Angs.		
11724-110	Catalyst, Experimental	35.5	119	0.13	124.9	44.1	38.3	30.2	517	1.68
11724-111	Catalyst, Experimental	44.2	105	0.11	120.9	44.5	39.7	30.2	446	1.95
11724-112	Catalyst, Experimental	55.1	73	0.09	128.3	48.4	52.0	30.4	290	2.31
11724-114	Catalyst, Std. Lab.	31.6	136	-	-	-	-	-	363 ^{b)}	1.54
12-MEM-403	Catalyst, Std. Plant	31.7	103	0.12	102.1	44.7	43.1	31.7	403	1.58
10891-61	Alumina Support	-	278	0.23	-	-	-	-	-	1.02
11724-51 ^{a)}	Catalyst, Std. Lab.	31.2	133	0.13	107.4	40.1	36.1	28.7	470	1.52

a) Made earlier²⁾; for comparison purposes.

b) This analysis was performed in Houston, while the other chemisorption analyses were performed in Emeryville with different equipment and personnel. Houston values are consistently lower than those determined in Emeryville but are presently considered to be more reliable.

APPENDIX I

EXPERIMENTAL

Raw Materials

The standard support, Reynolds RA-1 alumina, is of high purity and contained the following levels of impurities: SiO_2 , 0.06%; CaO <0.01%; Na_2O , 0.5%; TiO_2 , 0.005%; Fe_2O_3 , 0.03%; So , 0.03%; L.O.I., 6.24%; Al_2O_3 , 93.1% (by diff.). After washing and attriting the alumina the sodium content was lowered to 0.06%.

The chloroiridic acid (iridium tetrachloride) as supplied by Matthey Bishop must by specification contain no more than the following levels of impurities, based on iridium. Na , 0.10%; SO_4 , 0.20%; Fe , Cu , Cr , Ni , Pb , Sn and Ag <0.02%, each; other platinum metals <0.5% each; and total <1.0%.

Preparation of Catalysts

Catalyst preparation consists of essentially three steps:

1. The alumina support is impregnated with an aqueous solution of the iridium salt, dried, and heated to decompose the salt and convert it into a water-insoluble form. The impregnation and decomposition steps are repeated until the desired amount of iridium is deposited.
2. After the final impregnation/decomposition step the material is then treated with hydrogen at an elevated temperature to reduce the iridium to the metallic state.
3. The freshly produced catalyst is then exposed to air under controlled conditions.

The standard laboratory and plant preparative procedures are qualitatively the same except for the method of carrying out the drying/decomposition step.

Variation of iridium level in the experimental catalysts was effected by performing different numbers of impregnation/decomposition steps rather than using different concentrations of iridium salt in the impregnation solution.

APPENDIX II

Test Methods

Pore Volume Distribution

Pore volume distributions and surface areas are calculated from nitrogen adsorption isotherms measured with the aid of volumetric gas and sorption apparatus, the Aminco "Adsorptomat." ³⁾ This instrument, which is based on the design of Ballou and Doolen⁴⁾ automatically measures the amount of nitrogen adsorbed by a weighed sample at -196°C as a function of relative pressure over the range 0.01 to 0.995. The isotherm data are reduced by the method of Barrett, Joyner and Halenda⁵⁾ as modified by Emig and Hoffman⁶⁾ to obtain a cumulative pore volume distribution over the range of 16 to 850 angstroms. Volumes of pores between various size boundaries are calculated and plotted as functions of the average size. Several mathematical properties are computed for the distributions of both the volumes and areas of pores with respect to size. These include the weighted average, where the weighting factor is the volume or area of pores having diameters in a certain narrow range. The median value is the diameter exceeded by that for pores containing half the volume or area of the total sample. The computations and plot are made with the aid of a computer. Many assumptions are involved in this and other methods for the determination of pore volume distribution in this pore size range and no general statement can be made about precision and accuracy.

Surface Area

Surface areas are determined from the amounts of nitrogen adsorbed (using the Aminco Adsorptomat) by the sample at -196°C at several relative pressures in the range 0.05 to 0.3. The least squares estimates of the parameters of the Brunnauer-Emmet-Teller⁷⁾ equation which represents these data are found numerically and used to calculate the surface area of the sample. Precision of the surface area values is ± 2 percent.

Hydrogen Chemisorption

The amount of hydrogen chemisorbed by a weighed sample is measured by the dynamic method of Nelson and Eggertsen.⁸⁾ The apparatus used consists of a sample cell, thermal conductivity bridge, recorder and associated equipment as needed to pass gas over the sample under various conditions. The sample is reduced in hydrogen at 500°C and then cooled to 0°C in an argon stream containing 1 percent hydrogen while the composition of the exit gas is recorded. Hydrogen is taken out of the gas stream by chemisorption in this step. After the chemisorption is complete, as shown by the return of the gas composition to its original level, the sample is heated to 500°C to release the chemisorbed hydrogen. The amount evolved is measured by comparing the area under the peak in the composition-time curve to a calibration curve prepared from areas obtained by the addition of known amounts of hydrogen to the gas stream. The precision is ± 5 percent. The accuracy has not been established.

Crush Strength

A ten-gram quantity of support or catalyst is poured into a heavy-walled stainless steel cylinder of internal dimensions 0.875 inches diameter and 1.5 inches depth. A stainless steel plunger 3 inches in length and machined to smooth-sliding diameter is inserted into the cylinder and assembly is placed in a hand-operated hydraulic press. A force of 375 pounds (625 psi) is applied, held for 10 seconds, and released.

The compressed sample is removed and sieved in a 3-inch diameter U.S. Standard sieve (W. S. Tyler Company, manufacturer). The fraction retained on the sieve next greater in number (next smaller in screen opening) than the greater number sieve defining the original sample of support is recorded as Percent Survival.

Bulk Density

Packed bulk density, B.D., is determined by weighing a quantity of support or catalyst into a graduated glass cylinder to determine its volume. (In the standard procedure for Shell 405 Catalyst, 200 g of catalyst is weighed into a 250cc graduate; for this program, because of lesser amounts available, the total amount of support or catalyst prepared was weighed into a 100cc graduated cylinder.) The bottom of the cylinder is tapped for 3 minutes and the volume of material is then noted. Bulk density is reported on a dry basis, i.e., corrected for loss on ignition (L.O.I.) and calculated as follows:

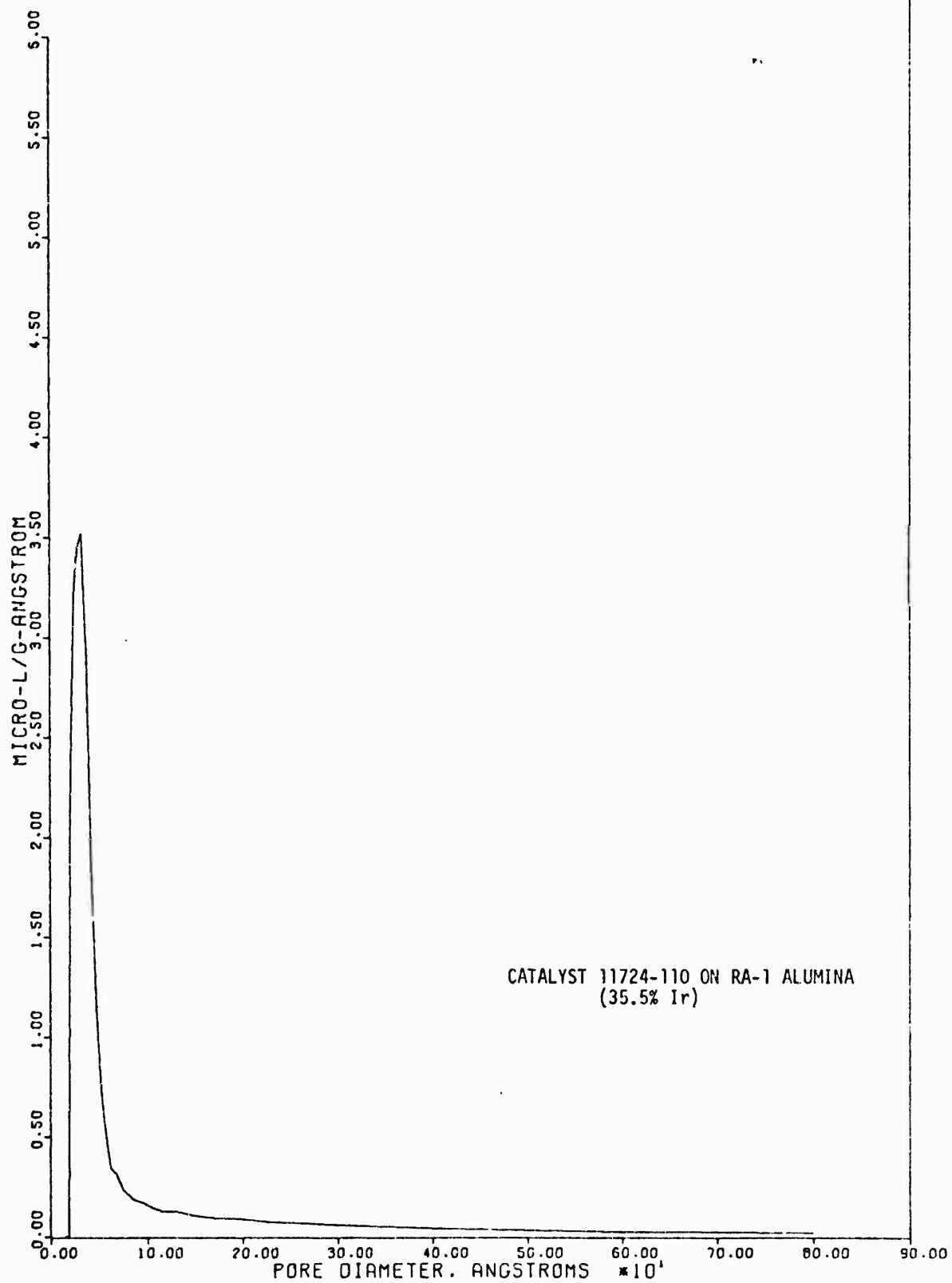
$$\text{B.D. (dry basis)} = \frac{\text{Weight} - \text{Weight (L.O.I./100)}}{\text{Volume}}$$

(L.O.I., %w, is determined by heating a weighted (1-2g) sample of support in a small porcelain crucible at approximately 700°C for 30 minutes, cooling in a desiccator and reweighing).

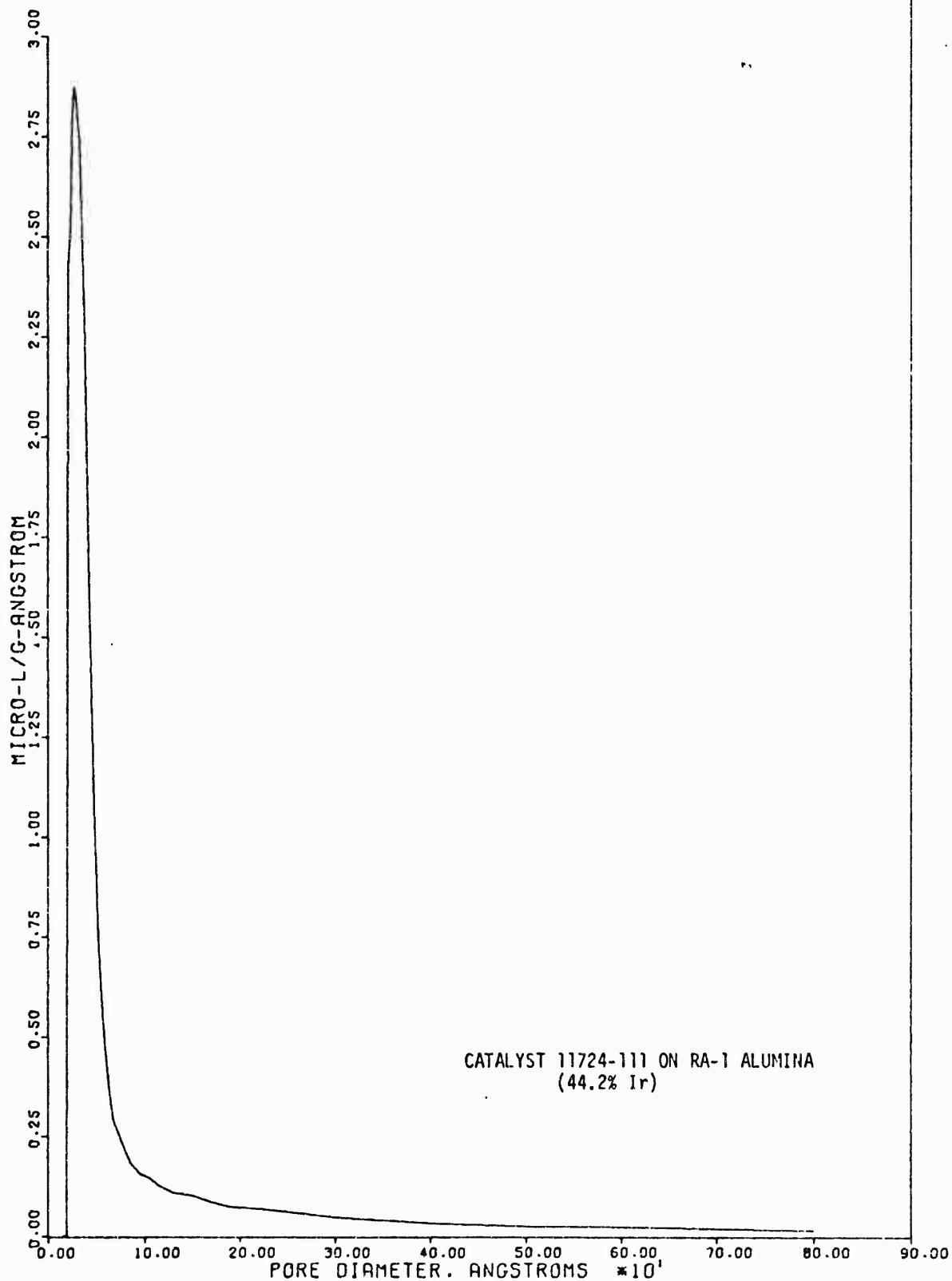
APPENDIX III

Graphs of BET Nitrogen Adsorption Data Output-Pore
Diameter as a Function of Specific Pore Volume Per
Unit Diameter

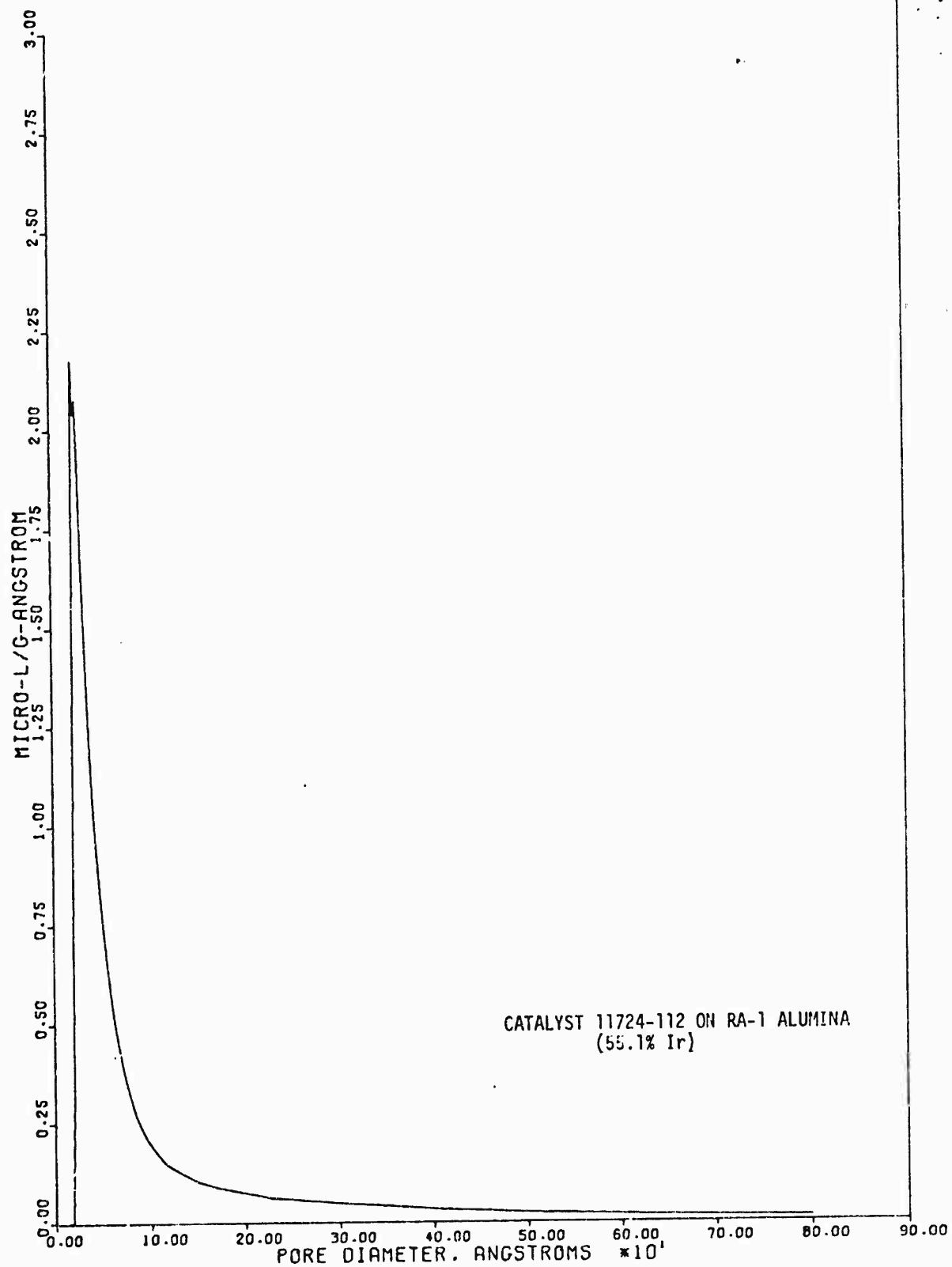
11724-110 36 PER CENT



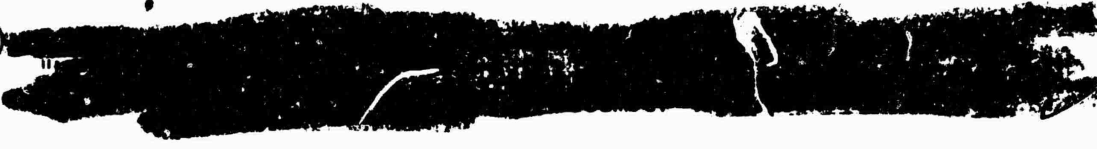
11724-111 45PERCENT



11724-112 55PERCENT



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